POTENTIAL SHORT-TERM TECHNIQUES FOR THE PRESERVATION OF CATTLE HIDES

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INTRODUCTION

Publication of increasing numbers of methods for short-term preservation of cattle hides suggest that short-term preservation should be defined so that these methods could be compared. We propose that the term "preservation" be defined not only as the retention of leather-making properties, but also as microbiological control, *i.e.,* reduction or elimination of microbial contamination. Using these criteria for preservation, we propose that short-term preservation be defined as "that period of preservation extending from hide removal to seven days." From eight days to four weeks would be "extended short-term preservation" and over four weeks, "long-term preservation."

The primary objective of our studies of various methods of hide preservation is to find economical ways to alleviate the pollution problem caused by the disposal of the large quantities of salt used in conventional curing procedures. A reliable short-term preservation which accomplished this aim would provide the tanner with a useful starting material as an alternative to green hides, which must be processed within one or two days. Although short-term preservation would not eliminate completely the need for salt-cured hides, it could be useful to a large segment of the hide-processing industry.

Several methods for holding fresh hides for a short time have been proposed. Cordon *et al.* (1) and Benrud (2) used a benzalkonium chloride treatment for fresh hides which might be delayed for a day or two before going into a salt cure. Money (3) studied a number of approaches to holding fresh hides for a short time with the purpose of by-passing the use of salt curing, which she indicated was costly and sometimes unnecessary. She found that fresh hides, treated with a spray of concentrated sodium chlorite or soaked in a dilute solution of sodium chlorite plus sodium pentachlorophenate, could be held up to six days before processing. Cutting and Scroggie (4), using the concentrations of sodium chlorite and sodium pentachlorophenate recommended by Money (3), preserved hides for five days. Nandy and Sens (5) used a soak of one percent paludrine and preserved hides for up to 32 days, but the method was considered uneconomical. George and Krishnamurthy (6) used zinc chloride and sodium pentachlorophenate as a precure treatment and preserved hides for seven days.

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Preservation of hides at ambient temperatures is a complex problem. Table I lists some of the treatment variables and Table II some of the hide variables that affect preservation. Cost also must be considered as a factor in terms of commercial acceptability. Our approach to hide preservation has been to use: (*a*) an acidic pH, (*b*) a low float to increase the solution concentration of all the ingredients used, and (*c*) low cost antimicrobial chemicals, such as Dextraset UN‡ and sulfite salts.

TABLE I

TREATMENT VARIABLES AFFECTING PRESERVATION

pH	Osmotic Pressure	Inhibitors
Type of acid Buffer capacity	Effect of float Types of salt	Types Dilution effect Inactivation
Treatment	**Time**	**Temperature**
Method (Dip, spray, agitate) Storage conditions	Hide removal to cure Time of cure Time of storage	Controlled Variable (High or low)

TABLE II

HIDE VARIABLES AFFECTING PRESERVATION

Microbes	Hide Composition
Bacteria, molds	Fat, protein, hair, species, age
Enzymes	**Hide Condition**
Tissue, blood, manure, microorganisms	Fresh, trimmed, washed, demanured, fleshed

This paper presents methods, using low-cost chemicals, that demonstrated the potential to provide short-term preservation and perhaps extended short-term preservation of fresh hides.

MATERIALS AND METHODS

Three preservation methods were studied. The first used two percent sodium bisulfite alone. The second used one percent sodium bisulfite with either one

‡Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

percent acetic acid or two percent sodium bisulfate as the acid source, and the third used 0.4 percent Dextraset UN (Dextran Chemical Corp., 50 percent N,N′-Bis(Methoxymethyl) Uron in aqueous solution) with the same acid sources. To all treatments, 0.03 percent Tergitol 15-S-9 was added. In all cases a 20 percent float was used and percentages were based on hide weight. Use of the low float resulted in relatively higher solution concentrations of all ingredients and therefore a higher osmotic pressure for a given amount of salt.

Small-scale experiments were carried out using 100-g. pieces of freshly flayed steerhide. Samples were kept frozen until needed. In each experiment the hide pieces were allowed to warm to ambient temperature and then added to the treatment ingredients in a one-quart mason jar. The tops were sealed and the jars then placed on a rotary shaker at 200 r.p.m. for 15 minutes. The samples then were stored in the jar at room temperature and samples were examined at different time intervals. The course of preservation was monitored by noting visual mold or bacteria, odor, hair tightness, and bacterial count.

Microbial counts were determined in the following manner. To the jar containing the 100-g. hide samples was added 500 ml. of sterile water. The sample was agitated for ten minutes on a rotary shaker at 200 r.p.m. and the liquid decanted into a sterile container. This procedure was repeated and serial dilutions then were made on the combined washes. Standard method agar plates were innoculated in duplicate for each dilution. Microbial colonies were counted after two to three days at room temperature.

Immediately after the hide samples were washed for bacterial counts they were submerged for three days in a 400-percent float containing ten percent lime, 0.25 percent sodium sulfhydrate, and 0.25 percent sodium sulfide, and then examined for hair removal and grain damage.

The large-scale experiments used freshly flayed hides both before and after washing, fleshing, and demanuring. Preservative treatments were applied by tumbling in a stainless steel drum for 0.5 hour. Controls were commercially brined hides or matched sides. Bacterial counts were carried out by a washing procedure similar to that used with small pieces with appropriate dilutions. Hides that were processed into the crust and into finished leather were evaluated by the tanner and by several physical tests.

Tensile strength was determined by following the official methods of ALCA (7). Relative stiffness measurements followed the techniques of Witnauer and Palm (8) and the ASTM standards (9). The SATRA Lastometer Mark II was used for the SATRA Grain Crack test. This test followed the methods of the International Union of Leather Chemists' Societies, where it is called the "Ball Burst Test" (10, 11). The SATRA results are given the following interpretation. An extension at grain crack of seven mm. or more should give leather satisfactory for lasting in most cases. A result less than six mm. represents leather that is below standard and unsuitable for lasting.

RESULTS AND DISCUSSION

It is well documented that hides can be held only for a short time before deterioration sets in. An experiment was conducted to determine how long fresh hide pieces could be held without preservatives under our experimental conditions. Table III demonstrates the effect of storage time on washed, fleshed, and demanured fresh hide samples. After 48 hours in the covered quart jars at room temperature, the odor of the hide pieces was bad, the hair was loose, and the

TABLE III

EFFECT OF STORAGE TIME ON PIECES OF FRESH STEERHIDE*

Time of Storage (Hours)	Bacteria per Gram Hide (Millions)	Hair Tight	Odor	Visual Mold	After Liming	
					Hair Loose	Grain Damage
Fresh	5.4	Yes	Normal	No	Yes	None
24	1,900	No	Bad	No	Yes	None
48	3,500	No	Bad	No	Yes	None
72	5,600	No	Bad	No	Yes	Yes
96	6,000	No	Bad	No	Yes	Yes

*The samples came from a hide that was washed, fleshed, and demanured. The samples were stored in sealed quart jars at ambient temperatures.

bacterial count was in the billions per gram of hide. However, after liming, the sample showed no obvious damage as evidenced by holes in the grain or excessive flaccidity. After 72 hours of storage, grain damage was visible after liming.

Preliminary experiments with small hide pieces were used to determine the conditions to be used for the initial side and whole hide experiments. A more complete study of these preservation methods will be published later.

Table IV shows the effectiveness of the three preservation methods on washed, demanured, and fleshed black steer sides. Commercially brined matched sides were compared with the corresponding treated sides. All three treatments effectively held bacterial load per gram of hide to levels below those of the brined controls. In addition, no mold growth was observed on any of these samples. Matched sides of the finished leather were not compared because several sides were lost in the tanning operation.

Table V demonstrates the effectiveness of these preservation methods on a more difficult substrate, full hides, from freshly flayed black steers, which were neither washed, demanured, fleshed, or trimmed. The acid source was $NaHSO_4$. A count of a fresh hide sample, which was relatively free of manure, had an initial inoculum of 30 million bacteria per g. of hide. With no control, as demonstrated in the first experiment (Table III), this count could move rapidly into

TABLE IV

EFFECTIVENESS OF PRESERVATION ON WASHED, DEMANURED, FLESHED SIDES

Hide Treatment*	Storage Time (Days)	Odor	Bacteria per Gram Hide
(1) 2% $NaHSO_3$	10	SO_2	1,800
Brined†	9	Phenolic	510,000
(2) 1% Na_2SO_3 + 1% HOAc	10	SO_2	1,700
Brined†	9	Phenolic	160,000
(3) 0.4% Dextraset UN + 1% HOAc	10	HOAc	97,000
Brined†	9	Phenolic	162,000

*Preservation solution was applied by agitation at 15 r.p.m. for 0.5 hr. in a stainless steel drum. Hides were stored along with the float in covered plastic containers at room temperature.

†Brined matched side.

TABLE V

EFFECTIVENESS OF PRESERVATION ON UNWASHED, UNFLESHED, UNTRIMMED HIDE

Treatment*	Storage Time (Days)	Odor	Bacteria per Gram Hide
2% $NaHSO_3$	14	SO_2	160,000
1% Na_2SO_3 + 2% $NaHSO_4$	14	SO_2	740,000
0.4% Dextraset UN + 2% $NaHSO_4$	8	Cabbage	600,000
Brined hide	14 (50°F.)	Phenolic	5,900,000
Fresh sample (Manure-free)	Freshly flayed	Normal	30,000,000

*Preservation solution was applied by agitation at 15 r.p.m. for 0.5 hr. in a stainless steel drum. Hides were stored along with the float in plastic bags at room temperature.

the billions. After 8–14 days, the preserved samples showed counts that are at least 98 percent lower than the original inoculum (Table V). The commercial brined hide control had a bacterial count of 5.9 million. In terms of bacterial numbers, therefore, each of the three preservative methods kept the hides under better bacterial control than the brine curing.

After the bacterial counts were set up, the hides were processed into upholstery leather at a tannery. In the crust condition all treated hides were considered satisfactory and the tanners made the comments listed in Table VI. The sulfite

treatments were best for mellowness, break, and feel; leather from the Dextraset UN treatment seemed strongest, and the brined control, although satisfactory, had a comparatively empty feel.

Microscopic examination (Table VI) showed that leather made from hides treated with Dextraset UN had many hair roots in the corium as compared to relatively few for all the other treatments; this indicated that the Dextraset UN

TABLE VI

TANNERS' COMMENTS ON LEATHER IN THE CRUST*

Hide Treatment	Break	Tensile	Feel	Mellowness	Microscopic Examination for Hair†
2% $NaHSO_3$	Good	Acceptable	Good	Good	No hair in grain; some in corium
1% Na_2SO_3 + 2% $NaHSO_4$	Good	Acceptable	Good	Good	Same as above
Brined hides	Acceptable	Acceptable	Empty	Acceptable	Same as above
0.4% Dextraset UN + 2% $NaHSO_4$	Acceptable	Strong	Bony, full	Acceptable	Some hair in grain; many roots in corium

*Leather made from experimentally preserved hides.
†Our observations.

made the hair somewhat more resistant to removal. Also, the full feel of leather from the Dextraset UN treatment may indicate that the treatment fixes hide substance and makes it less likely to be removed in liming and bating.

Table VII gives physical test data on the tensile strength and relative stiffness of the hides in the crust condition. The tensile strengths on the Dextraset UN treated and the brine-treated hides were about the same, and both were higher than the tensile strengths on the sulfite-treated hides. The stiffness test showed that the Dextraset UN-treated hide was the stiffest, followed closely by the brined hide. The sulfite-treated hides were much less stiff, which was reflected in their evaluation as the mellowest of the group.

Each of the crust samples then was finished into upholstery leather. All were considered commercially acceptable. Table VIII reports physical test values on the finished leather. The tensile strengths all followed the same pattern as in the crust. The SATRA grain crack showed extension values that fell well above acceptable levels for all samples tested and indicated that all these leathers would be satisfactory for lasting.

These results demonstrate that the three preservation methods described using low cost commercially available chemicals are potentially useful methods for

TABLE VII

PHYSICAL TEST DATA ON LEATHER IN THE CRUST*

Hide Treatment	Location	Tensile**			Relative Stiffness	
		Elongation (%)	Break Load (lbs.)	Tensile (p.s.i.)	Degrees parallel	Twist perpendicular
2% $NaHSO_3$	Belly	24	38	1650	135	125
	Butt	69	34	1230	205	145
1% Na_2SO_3 +	Belly	33	37	1410	140	200
2% $NaHSO_4$	Butt	44	29	1195	160	155
0.4% Dextraset	Belly	51	47	1980	150	310
UN + 2% $NaHSO_4$	Butt	57	44	1630	320	210
Brined hide	Belly	29	47	1930	160	240
	Butt	42	36	1420	195	180

*Leather made from experimentally preserved hides.
**Parallel to the backbone.

TABLE VIII

PHYSICAL TEST DATA ON FINISHED LEATHER (BUTT AREA)

Hide Treatment	Tensile**			SATRA Grain Crack	
	Elongation (%)	Break Load (lbs.)	Tensile (p.s.i.)	Extension (mm.)	Load (kg.)
2% $NaHSO_3$	46	39	1720	9.07	22
1% Na_2SO_3 + 2% $NaHSO_4$	46	32	1500	9.13	19
0.4% Dextraset UN + 2% $NaHSO_4$	40	57	2310	9.57	26
Brined hide	53	54	2190	9.24	23

*Leather made from experimentally preserved hides.
**Parallel to the backbone.

preserving fresh hides without the use of sodium chloride. Dextraset UN has been in commercial use for over ten years and it is assumed by the manufacturer to be nontoxic and not a pollution problem. The methods using sulfite salts introduce only small amounts of sodium bisulfate and sodium sulfite relative to the amount of sodium chloride used in brine curing, and most of the sulfite and sulfate anions would be expected to precipitate in the lime as the insoluble calcium salts. It was significant that even unwashed, unfleshed, and untrimmed hides were preserved for eight to 14 days and then could be made into commercially acceptable leather. Using our proposed definition of preservation, this constitutes extended short-term preservation. At present we do not have evidence that this is the lower limit attainable by these methods. However, these experiments have

not been conducted on a large scale and it is not certain that these few experiments can determine accurately the length of preservation attainable. Therefore, we conservatively claim only to have achieved short-term preservation and will wait for pilot-plant studies to determine whether longer preservation can be achieved by these methods.

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DISCUSSION

MR. GUY MOBERG (Dennison Hide Co.): I want to thank you, Bill. I think this is a very timely subject, in fact, one somewhat overdue for action. We have become quite aware of the problems in processing fresh hides and the possibilities of the short cure. There has been considerable effort expended in the methods of hide curing and we have already made enormous improvements. However, we have far too long overlooked the one important factor which has been brought to our attention by tannery effluent problems. This is the traditional sodium chloride hide cure. Mr. Hopkins' paper today is a start and indicates the interest of the Eastern Regional Research Laboratory of the USDA in this subject of short-term hide cure. To re-emphasize Mal Battles' remarks of this morning, I would like to say to Joe Naghski that I hope you have this subject of hide cure listed as a top priority in your laboratory. We have allowed time to pass us by and soon this problem is to be staring us right in the face. To start

the questions off, I would like to ask Bill (Hopkins) if he has gone into the possibility of the type of application we would use for the Dextraset and also, were there any changes in processing required by the tanner as against his normal procedures using brine-cured hides?

MR. W. J. HOPKINS (Eastern Regional Research Laboratory, USDA): In answer to your first question, our approach initially was to screen preservatives. Money recently gave a paper on short-term hide preservation, and the applications used were a spray treatment and also a soak. In both cases, discounting the costs of the chemicals used, these approaches were considered to be economically satisfactory, and overall were considerably less costly than a conventional salt cure. Does that answer your first question? As far as changing the tannery hide processing is concerned, we did run some full sides through a tannery. One of the factors we have to consider is that when we give a tanner a sample hide, he does not change his process to meet any special needs of our experimental samples. The raw stock has to go through according to his standard procedure. The answer then is that there were no changes in the tanning process to accommodate the short-term preserved hides.

DR. PETER R. BUECHLER (K. J. Quinn Co.): Bill, I was wondering how much SO_2 odor there was from the sulfite treatment and how troublesome this condition might become if a large number of hides were treated at one time?

MR. HOPKINS: Yes, the SO_2 odor could be troublesome. This treating material in an acid medium could be a problem. We have some indications that pH and concentration can affect this aspect of the hide treatment. The concentrations that we presented here at this time probably might be higher than would be used in normal production. We are continuing this work in order to obtain more data. We have noticed many interesting things about hide preservation without salt. We didn't know anything in the beginning but we have learned a lot. We used sulfite because it is a well-known preservative and it is cheap.

MR. DAVID R. SMALL (Saco Tanning Corp.): On the question of the formaldehyde reactant to preserve hides and its action on the hair roots, would you please elaborate on this effect a little more? Are the hair roots, which could be tanned in or pinched in by the formaldehyde preserving action, a factor that can be ignored in later processing? Is this a difficulty that can be overcome in subsequent processes, or are these hair roots just to be there in the leather?

MR. HOPKINS: On the samples that we had processed the tanner did not find objectionable hair roots. In the hair burning process, in some cases, hair roots may be left in the hide. We have seen samples of leather which had hair roots in the corium and this was commercial quality material. Perhaps someone in the audience may now give us some more information on this point.

DR. HARLAND H. YOUNG (Research Advisory Service Inc.): With respect to hair roots, I am wondering whether or not in the use of sulfur dioxide at a

2.0 percent level, presumably 2.0 percent on the hide weight basis, when sodium bisulfite or SO_2 are added, at least some of the sulfide would be inactivated to produce colloidal sulfur. That condition may cut the SO_2 odor. I don't know whether this was compensated for or not. Another comment I would like to make is that one of the specific enzyme poisons, if you are concerned about enzymes, whether generated by bacteria or other sources, is the zinc ion. You will recall that the glue industry uses 1.0 percent zinc sulfate to hold them up for the so-called Keep Test, which is 100 hours at 98°F. at 100.00 percent humidity. That may well be an additive to consider. I don't mean at the 2.0 percent level, but as an additive to cut down the enzyme action. Probably you have read of people pounding galvanized nails into elm trees in order to knock off the enzyme allegedly left by the Dutch Beetle or the Elm Beetle, as the case may be. I do believe that, as far as the sulfur dioxide is concerned, we did, some years ago, have a protest on a shipment of hides to Yugoslavia because of hair slip and bad odor. These hides were conventionally brine-cured with "Safety Salt" and with an added preservative of a halogenated phenol. In order to bolster that treatment we added about 5.0 to 8.0 percent, on the Safety Salt weight, of sodium bisulfite. We made the situation worse, I am sorry to say. We had more trouble after the sodium bisulfite addition, and I don't know why. This information is given for what it is worth.

MR. HOPKINS: Sodium bisulfite was the additive?

DR. YOUNG: Yes. Sodium bisulfite was added to the Safety Salt. That was for one lot of hides. In any of these tests, I think that we should all consider almost statistical data because there are such huge variances between the raw stocks from various suppliers.

MR. HOPKINS: Thank you for your comments. Maybe by the time the bisulfite was added it did not affect the enzymes that were present in the hides. Possibly if a high concentration of enzymes is allowed to build up it might be a problem to control them.

DR. YOUNG: It was a one-shot deal. My comment was to give my experience with the bisulfite treatment.

MR. JAMES CHITTENDEN (Iowa Beef Processors Co.): I notice that you kept the hides in a bag. Is that correct? With the float? Is this necessary?

MR. HOPKINS: No, we don't think so. However, in this case the hides were kept in a covered plastic box. In another test they were kept in a double plastic bag, with the float. We think they can be kept without the float.

MR. CHITTENDEN: Was there any attempt to determine what kind of shrinkage you might have encountered during the storage period?

MR. HOPKINS: We don't have data on that.

MR. MOBERG: I would like to ask you, Bill, has there been any study made as to the appropriate raw hide pH level that would have an effect on the removal of hair?

MR. HOPKINS: No, we haven't done too much work in this area. However, could you rephrase the question, please? Perhaps I did not get your meaning.

MR. MOBERG: I find that when we get down in the acid range the hides are apt to develop a tight hair situation.

MR. HOPKINS: Do you feel that this could develop problems in later hair removal?

MR. MOBERG: Yes, especially when a hair-saving process is to be used, to save the hair.

MR. HOPKINS: We examined the leather samples out of a hair-saving lime. We found no problems with the removal of hair from hides after the use of our preservative methods on the hides. The lime was used because it is a harsh condition to expose the hide to, and the hide would have to go through lime in the normal processing. We felt this would be a good criterion also to check the ability of the preserving methods to preserve the hide.

MR. MOBERG: Is there anyone in the audience who has had experience on this question?

DR. BUECHLER: In the older literature ("Acid Unhairing" by R. H. Marriott, *J. Soc. Leather Trades' Chemists,* **5,** 2 (1921)) there is a comment that you can unhair very effectively, in fact much more effectively, in the acid state rather than in the alkaline state. Just by reducing the pH, you can get unhairing. On the other hand, one of the big problems is that the hide swelling is much more extensive with acid unhairing and that is why it has not been adopted commercially.

MR. MOBERG: Thank you. Now, if there are no more questions I want to thank you, Bill, for a very good paper.